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INNOVATIVE BIOLOGICAL SOLID-PHASE (OR LAND) TREATMENT OF PETROLEUM HYDROCARBONS (PHCS) AT THE UNITED STATES NAVY'S CRANEY ISLAND FUEL TERMINAL IN PORTSMOUTH, VIRGINIA

[1]Paul E. Flathman, [2]Gregory P. Hatchett, [3]Jeffrey C. Weatherly, [1]John H. Carson, Jr.
[3]James M. Wrona, [1]Douglas E. Jerger, [1]Paul R. Lear, [1]Patrick M. Woodhull, and [4]James L. Brown

[1]OHM Remediation Services Corp., Findlay, OH 45839-0551 USA
419-425-6133/419-425-6031 (fax)
[2]Department of the Navy, Atlantic Division, Naval Facilities
Engineering Command, Norfolk, VA 23511-2699
[3]OHM Remediation Services Corp., Glen Allen, VA 23060
[4]OHM Remediation Services Corp., Trenton, NJ 08691-1904

ABSTRACT

Biological treatment was performed to remediate ~18,000 yd^3 (14,000 m^3) of petroleum hydrocarbon (PHC)-contaminated soil at a U.S. Navy land treatment facility. The soil was contaminated with Fuel Oil 535 which was a heavy, special grade fuel oil. The PHCs had weathered in place for 14 years prior to excavation and treatment. Most of the weathered product was contained in hard, hydrophobic clods up to several inches (centimeters) in diameter. Three innovative treatment areas (ITAs), i.e., ITA A (bacterial enzyme product), ITA B (selected bacterial mixture), and ITA C (oleophilic nutrient/selected bacterial mixture), were evaluated for increasing the rate and extent of biological treatment of the PHCs. The efficacy of those innovations was compared to conventional, mineral nutrient-amended land treatment. The rate of treating the PHCs in ITA C was approximately twice that of the other areas. With greater than an 80% reduction in PHC concentration in ITA C after 90 days of treatment compared to 67% reductions in the other ITAs and in the conventional treatment area (CTA) after 120 days of treatment, the benefit of the oleophilic nutrient/selected bacterial mixture for remediation of PHC-contaminated soil was demonstrated.

INTRODUCTION

In 1993, the United States Navy constructed and first tested a 600 ft x 1,000 ft (180 x 300 m), 14-acre (5.6 hectare), solid-phase (or land) treatment facility at the Fleet and Industrial Supply Center (FISC), Craney Island Fuel Terminal in Portsmouth, Virginia. The facility was designed to biologically remediate large volumes of PHC-contaminated soils obtained from Craney Island and other nearby Navy facilities. In 1994, under the U.S. Navy's Atlantic Division's (LANTDIV) Contract N62470-93-3032, Delivery Order 0016, OHM Remediation Services Corp. was contracted to remediate approximately 18,000 yd^3 (14,000 m^3) of PHC-contaminated soil transported to the facility from Site 13 at the Navy's FISC, Yorktown Fuels Division, Yorktown, Virginia.

Soil at the Yorktown facility had become contaminated with Fuel Oil 535. This was a heavy, special grade fuel oil that had been produced for the Navy by ARCO Petroleum Products Company. PHCs from tank still bottoms had contaminated loamy sand soil at the facility, and the PHCs had weathered in place for 14 years prior to excavation and treatment. Most of the weathered product was contained in hard, hydrophobic clods up to several inches (centimeters) in diameter. As determined by USEPA Method 418.1 (Total Recoverable Petroleum Hydrocarbons, Spectrophotometric, Infrared), total PHC (TPH) concentration in the soil averaged 1,200 mg/kg. As specified in the Virginia Solid Waste Management Regulations, the cleanup level at the site was 50 mg/kg TPH. A risk-based treatment variance for industrial locations later established the cleanup level at 1,000 mg/kg TPH.

The project objectives were to reduce TPH concentration to 50 mg/kg in a 120-day treatment period and to compare the effectiveness of three innovative treatment products to conventional treatment methods by being able to detect a 20% or greater difference in treatment with 80% confidence. Innovative treatment areas (ITAs) A (bacterial enzyme), B (selected bacterial mixture), and C (oleophilic nutrient/selected bacterial mixture) were constructed at the facility to evaluate three innovative products for increasing the rate of biological treatment of the PHCs. The efficacy of these innovations was compared to a conventional solid-phase control (Area D) after 120 days of treatment.

FIELD IMPLEMENTATION

Solid-phase (or land) treatment of hazardous waste is a managed technology that involves the controlled treatment of a waste in the upper soil zone. This treatment technology relies on the dynamic physical, chemical, and biological processes that result in the biodegradation, immobilization, or transformation of a hazardous waste to an environmentally acceptable level. Solid-phase treatment has been widely used throughout the world to treat petroleum industry and other industry wastes to acceptable levels.

In the 14-acre (5.6 hectare) treatment cell, the 18,000 yd^3 (14,000 m^3) of PHC-contaminated soil were spread to an average depth of 9.6 in (24 cm). ITAs A (bacterial enzyme), B (selected bacterial mixture), and C (oleophilic nutrient/selected bacterial mixture) were constructed at the facility to evaluate three products for increasing the rate of biological treatment of the PHCs. The efficacy of these innovations was compared to a conventional solid-phase control (Area D) after 120 days of treatment. Twelve tons (11 metric tons) of diammonium phosphate (DAP), $(NH_4)_2HPO_4$, was initially added to the soil in all areas of the treatment cell as an immediately available source of nitrogen and phosphorus to support microbial growth on the PHCs. On Days 30, 60, and 90, additional 12-ton (11 metric-ton) quantities of DAP were also added to the entire site. A schematic of the treatment cell is presented in **Figure 1A**. A Caterpillar SS-250 Soil Stabilizer and Reclaimer (Caterpillar, Inc.; Peoria, IL) and a Scat 482B Compost and Bioremediation Turner (Skat Engineering; Delhi, IA) were used to reduce the size of the clods, to mix the soil amendments, and to make the PHCs more available for aerobic biological treatment.

A sampling and analysis plan was developed which had the following objectives:

- To validate the attainment of the 50 mg/kg TPH cleanup level in soil at the site as required in the Virginia Solid Waste Management Regulations,
- To compare the effectiveness of three innovative treatment products to conventional treatment methods by being able to detect a 20% or greater difference in treatment with 80% confidence,
- To assure the maintenance of soil conditions conducive to enhanced microbial growth on PHCs, and
- To establish that leachate discharged from the treatment cell to the wastewater treatment plant at Craney Island would not adversely affect plant operations.

Samples were analyzed according to USEPA,[1-3] American Society of Agronomy/Soil Science Society of America (ASA/SSSA),[4-5] and American Public Health Association's *Standard Methods* procedures (**Table 1**).[6]

With the exception of ITA C, baseline sampling was performed on Day 0 prior to startup of the treatment cell. Interim samples were collected on Days 30, 60, and 90, and final samples were collected from the treatment cell on Day 120. In ITA C, baseline sampling was performed on Day 30. Innovative treatment in Area C was, therefore, evaluated over a 90-day period. Baseline samples in each treatment area were collected along an equilateral triangular grid (**Figure 1A**) according to USEPA procedures.[7-8] The maximum information from a fixed number of samples in a fixed area is obtained by maximizing the average distance between adjacent sample locations. The equilateral triangular grid affords the highest average spacing between sample locations and provides the maximum information about contaminant distribution.

TABLE 1. ANALYTICAL METHODS FOR MONITORING ANALYSES

Parameter	Analytical Method	
	Soil	Leachate
Total Petroleum Hydrocarbons (TPH)	USEPA 418.1	USEPA SW-846 M8015
Benzene, Ethylbenzene, Toluene, and *o*-, *m*-, and *p*-Xylene (BETX)	USEPA SW-846 8020	USEPA SW-846 8020
Oil & Grease	[1]NA	USEPA 413.1
Total Organic Halogens (TOX)	USEPA SW-846 9022	USEPA 450.1
Total Organic Carbon (TOC)	USEPA SW-846 9060	USEPA 415.1
pH	ASA/SSSA 12-2.6	USEPA 150.1
Available Mineral Nutrients		
Ammonium-Nitrogen (NH_4-N)	ASA/SSSA 33-3/33-4	USEPA 350.2
Nitrate-Nitrite-Nitrogen (NO_3-NO_2-N)	ASA/SSSA 33-3/33-4	[2]USEPA 352.1
Phosphate-Phosphorus (PO_4-P)	ASA/SSSA 24-5.1/24-5.3	USEPA 365.2
Potassium (K)	ASA/SSSA 13-3.3.1.2/13-3.3.3	USEPA SW-846 6010
Aerobic Heterotrophic Bacterial Population Density	SM 9215 B	NA
Soil Moisture Content	ASA/SSSA 21-2.2	NA

[1]NA = Not Analyzed
[2]NO_3-N

For each sampling event, a total of 26 and 120 sampling points were respectively collected in each ITA and in the CTA. On Days 0 and 120, for every 2 samples collected within each ITA, one composite sample was prepared for a total of 13 composite samples. For every 6 samples collected within the CTA, one composite sample was prepared for a total of 20 composite samples. Two duplicate samples were also collected and analyzed for TPH. One duplicate sample was collected from the CTA, and a second duplicate sample was collected from one of the ITAs. On Days 30, 60, and 90, those numbers of composite samples were respectively reduced to 2 and 6. In addition to TPH, baseline samples were also analyzed for BETX, TOX, TOC, pH, available mineral nutrients, bacterial population density, and soil moisture content. When baseline sampling was completed on Day 0, the soil was placed into windrows (**Figure 1B**) and the sampling plan was modified. A more detailed discussion of sample collection, windrow construction, and monitoring of the treatment cell has been previously presented.[9]

RESULTS AND DISCUSSION

Performance data has indicated that biodegradation of most chemicals in soil can be modeled using a first-order reaction rate or a mixture of first-order rates. First-order kinetics generally apply where the available

concentration of the chemical being degraded is low relative to the biological activity in the soil.[10] Biological treatment of TPH was modeled according to the following integrated form of the first-order model:

$$C(s,t) = C(s,0)e^{-k(s)t}$$

where,

C(s,t) = average TPH concentration (mg/kg) in treatment area s at time t (days),
C(s,0) = average TPH concentration (mg/kg) in treatment area s at time 0 (days),
k(s) = first-order rate constant (day^{-1}) for area s,
t = time (days), and
s = treatment area.

The first-order model was fit to the TPH data using the method of generalized linear interactive modeling (GLIM) for the purpose of estimating initial TPH concentrations and first-order rate constants for each area. GLIM models are a generalization of ordinary linear models that can incorporate several features often found in real modeling situations. A GLIM model, rather than ordinary nonlinear least squares regression, was required, because the error variance (i.e., variance of random deviations of observed concentrations from the "true" values) in TPH data was not constant but was an increasing function of average TPH concentration (**Figure 2A**). This phenomenon is quite common in environmental and other earth sciences data, particularly when the data is collected over a spatial domain, and is sometimes referred to as the "proportional effect."

Table 2 presents estimates of the contrasts in the first-order rates of treating the PHCs in the ITAs compared to the CTA control (Area D). Although the fitted first-order rate constants for ITAs A and B were slightly higher than that for the CTA, the differences were not statistically significant at the 0.01 level. The *p*-values for the rate differences for ITAs A and B were respectively 0.13 and 0.31. The rate contrast between ITA C and the CTA was highly significant ($p = 2.7 \times 10^{-6}$). Based on initial results, the model was refit by assuming the same rate of TPH degradation (but different initial TPH concentrations) for ITAs A and B as for the CTA. Random variation was modeled as having a distribution symmetric about 0 and a standard deviation proportional to the TPH concentrations predicted by the model. Studentized residuals from a GLIM model are ordinary residuals divided by the standard error of prediction and corrected for transformation bias. Studentized residuals from this model were plotted against model predictions for the purpose of assessing whether the error variance was correctly modeled and whether higher order model terms might be required (**Figure 2B**). Inspection of **Figure 2B**, indicated the absence of any trends which would indicate lack of fit. The studentized residuals were distributed symmetrically about the zero line, and their dispersion appeared to be independent of the predicted values.

Studentized residuals versus normal quantiles were plotted to assess the shape of the error distribution (**Figure 2C**). The studentized error distribution appeared to be symmetric (but not necessarily normal) except for the extreme tails which exhibited some skewness to the right. Extreme points on the plots in **Figures 2B and 2C** were labeled according to their corresponding area. **Figures 2B and 2C**, therefore, indicated that there were no patterns which would suggest that the model was deficient. The estimated first-order rate for ITA C was approximately twice that of the pooled estimate rate for ITAs A and B and for the CTA (**Table 3**). Test results for TPH and first-order model predictions with 95% confidence limits for ITAs A, B, and C and for CTA D as a function of time are respectively presented in **Figure 3**.

TABLE 2. COMPARISON OF FIRST-ORDER RATES OF BIOLOGICAL TREATMENT IN THE INNOVATIVE TREATMENT AREAS COMPARED TO CONVENTIONAL LAND TREATMENT (AREA D)

Treatment Area	Treatment	Difference in Rates (Day^{-1})	Standard Error	Z-Score	[1]p-Value
A	Bacterial enzyme	0.00206	0.00184	1.12	[2]0.131
B	Inorganic/trace organic nutrient and selected bacterial strain mixture	0.00091	0.00184	0.496	[2]0.310
C	Oleophilic nutrient/selected bacterial strain mixture	0.00989	0.00218	4.56	[3]0.000002744

[1]Probability that an observed difference (or a greater difference) in first-order rates of biological treatment could occur by chance under the null hypothesis

Null hypothesis states there was not a significant difference in first-order rates of biological treatment between conventional (Area D) and innovative treatment areas

[2]First-order rates of biological treatment for Areas A and B not significantly different than for Area D
[3]First-order rate of biological treatment for Area C significantly greater than for Area D

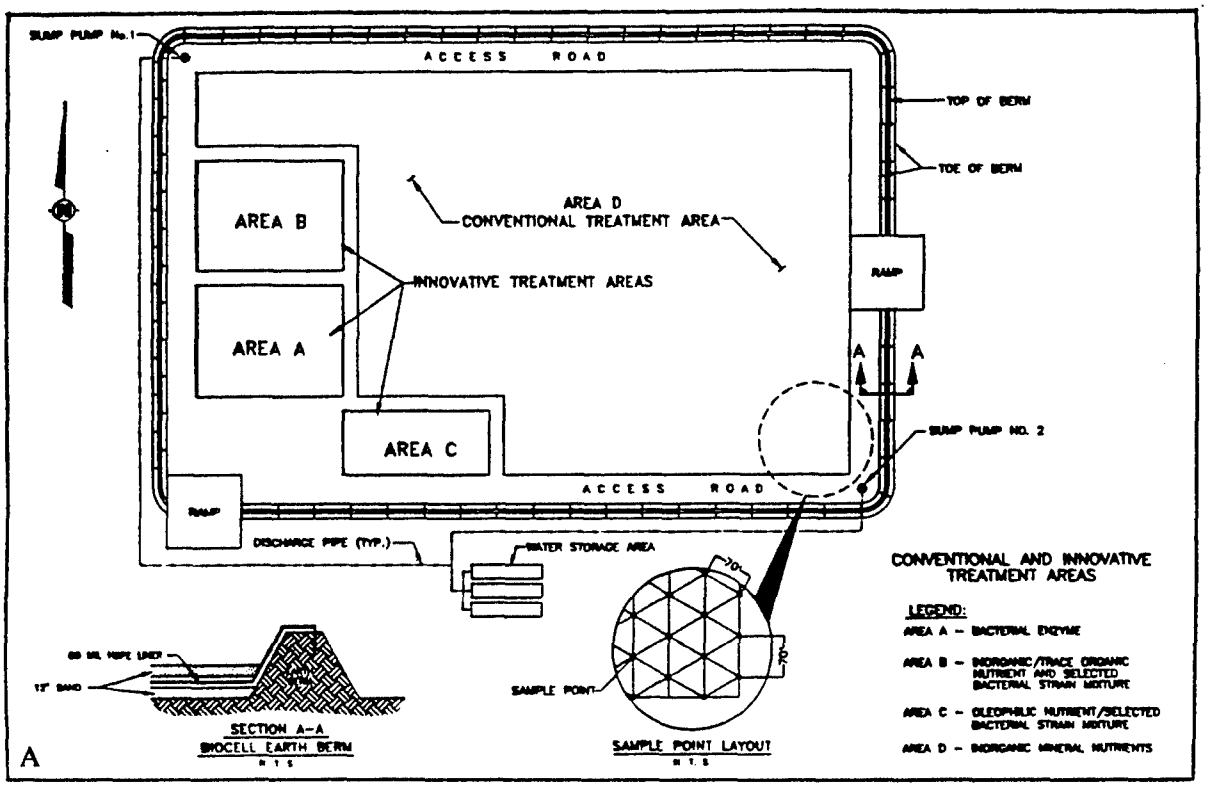
TABLE 3. FIRST-ORDER RATES OF BIOLOGICAL TREATMENT IN THE INNOVATIVE AND CONVENTIONAL LAND TREATMENT AREAS

Treatment Area	Treatment	K (Day^{-1})	Standard Error	95% Lower Confidence Limit	95% Upper Confidence Limit
A	Bacterial enzyme	[1]0.00928	0.000803	0.0077	0.0109
B	Inorganic/trace organic nutrient and selected bacterial strain mixture				
D	Conventional land treatment				
C	Oleophilic nutrient/ selected bacterial strain mixture	[2]0.0184	0.00146	0.0155	0.0213

[1]GLIM model refit with common first-order rate of biological treatment for Areas A, B, and D and with different initial concentrations for each area retained in the model

ITA A	C_0 = 741 mg/kg
ITA B	C_0 = 802 mg/kg
ITA C	C_0 = 943 mg/kg
CTA D	C_0 = 1,220 mg/kg

[2]First-order rate of biological treatment of TPH in Area C twice that of the other areas



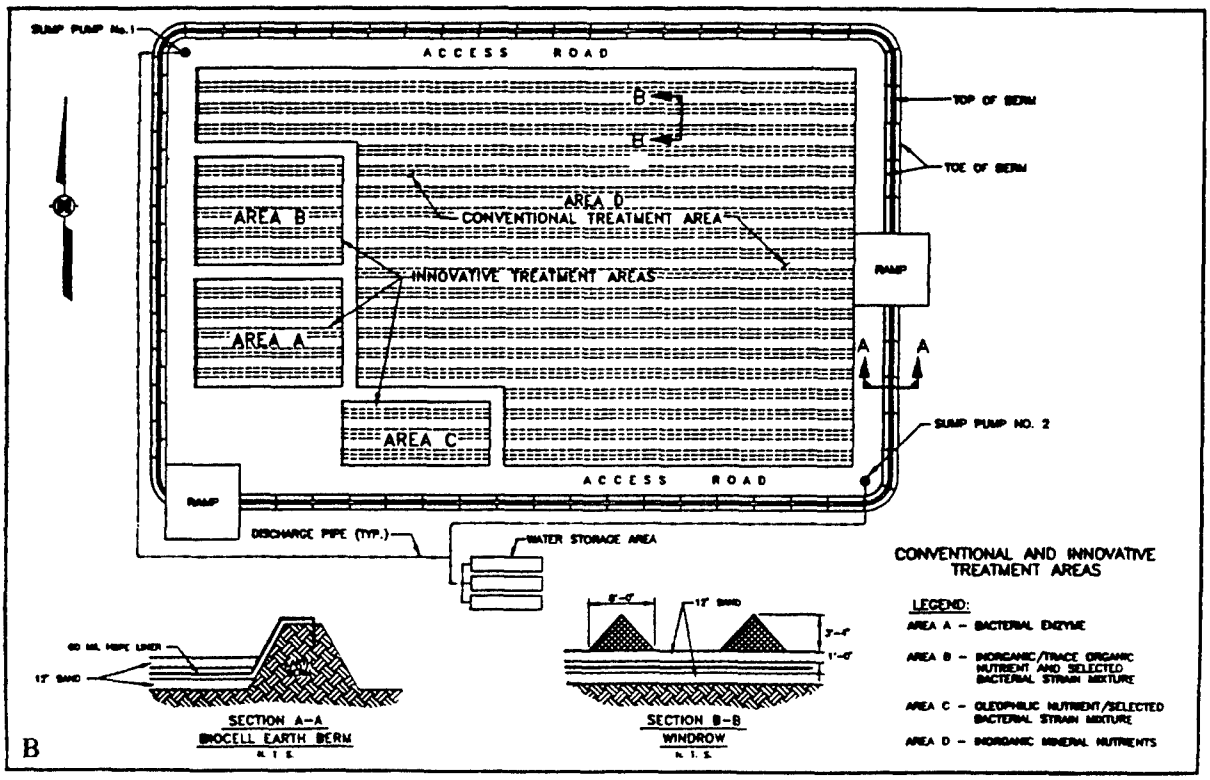


Figure 1. Land treatment cell and triangular grid sampling on Day 0 (A) and windrow construction for sampling on Days 30, 60, 90, and 120 (B).

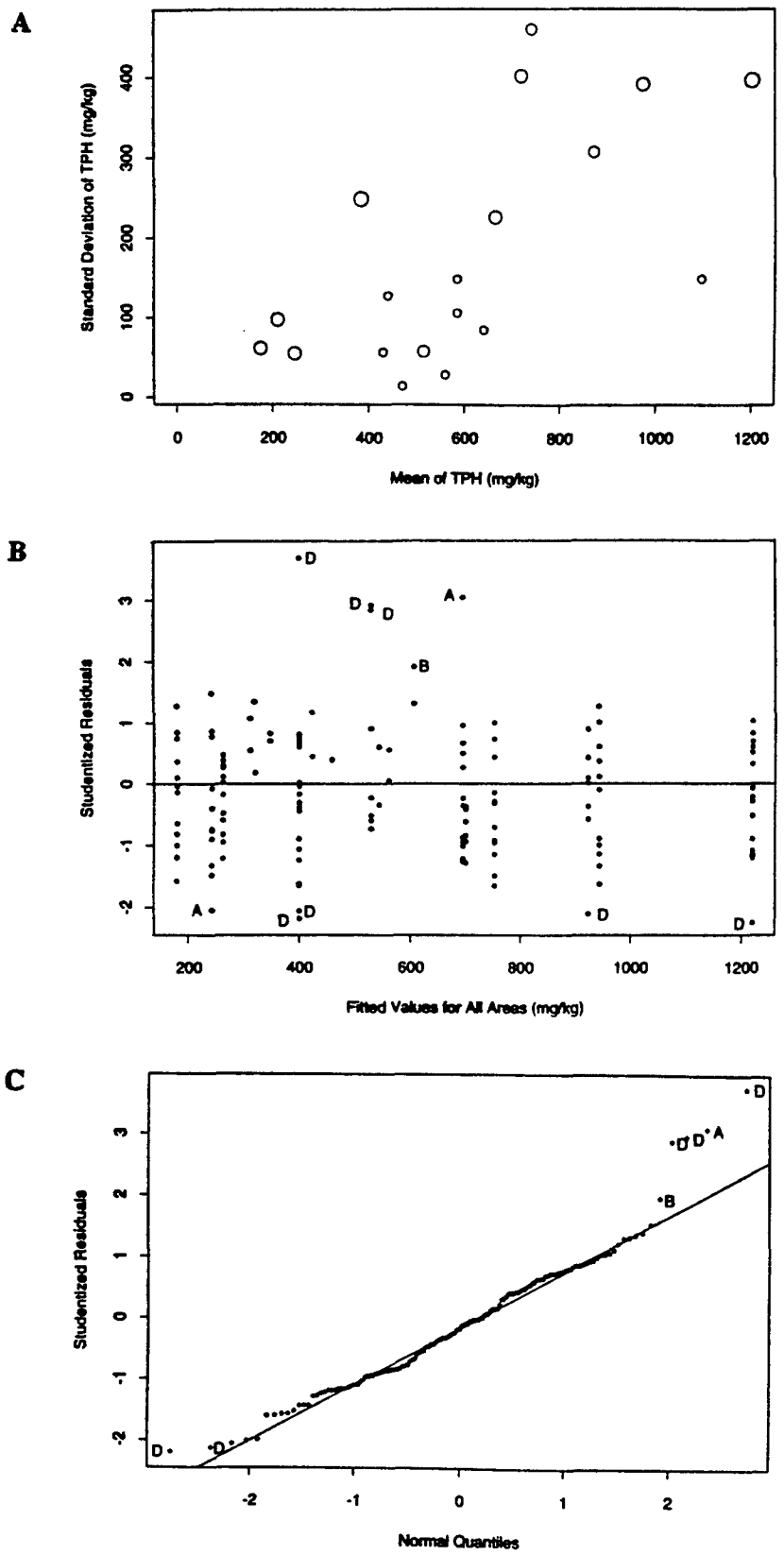


Figure 2. Diagnostic checking of the first-order model.

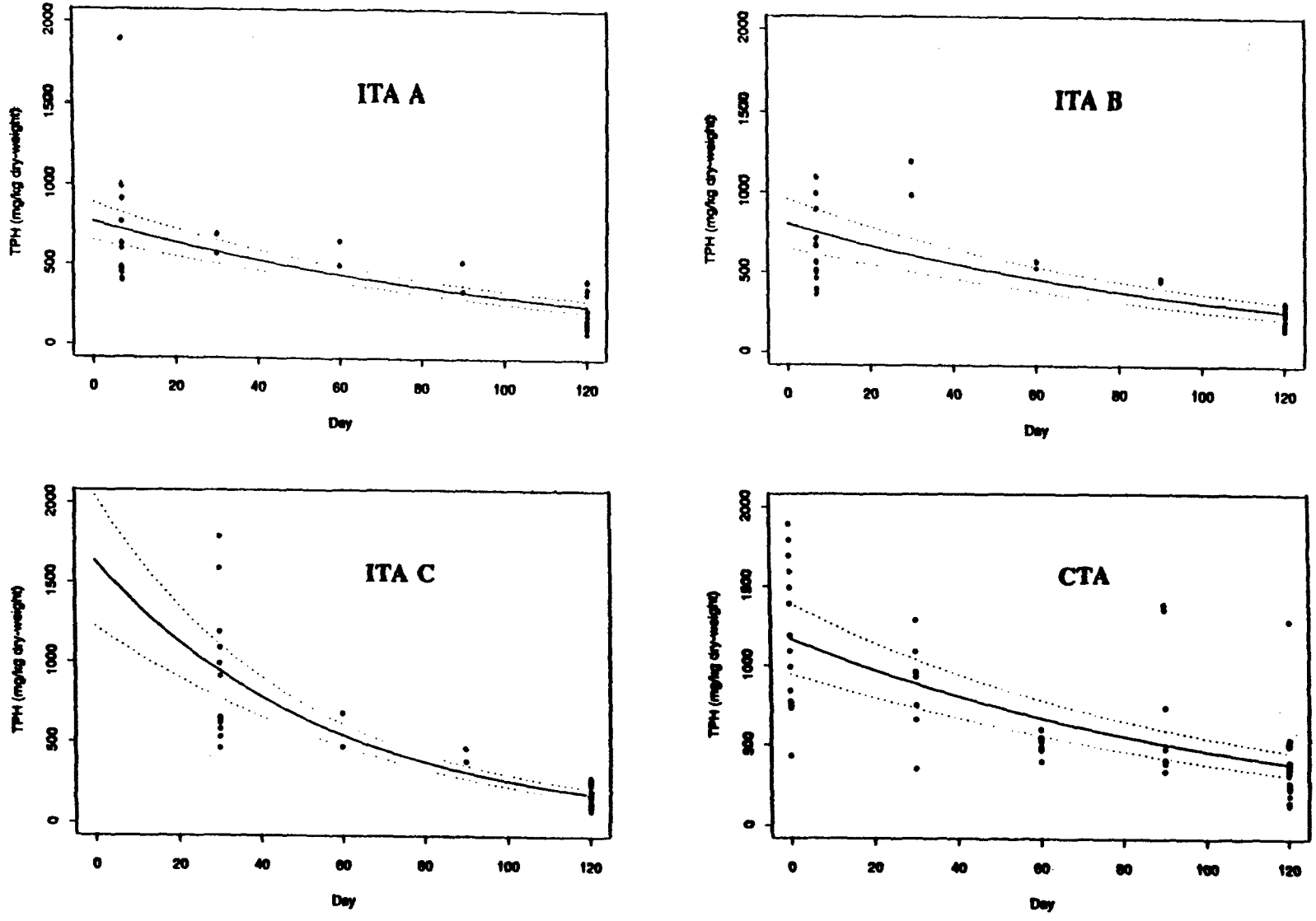


Figure 3. TPH concentrations and first-order model prediction with 95% confidence limits presented as a function of time for the ITAs and the CTA.

Table 4 presents the percent reduction for each area based on the final model and on the results of the initial and final sampling events. The extent of PHC treatment in ITA C was substantially greater than in any of the other areas. With greater than an 80% reduction in PHC concentration in ITA C after 90 days of treatment compared to 67% reductions in the other areas after 120 days of treatment, the benefit of the oleophilic nutrient/selected bacterial mixture for remediation of PHC-contaminated soil was demonstrated. The oleophilic nutrient / selected bacterial strain mixture evaluated in ITA C was developed by Eugene Rosenberg et al.[11] at Tel-Aviv University in Tel-Aviv, Israel through the financial support of Makhteshim Chemical Works Ltd (Beer-Sheva, Israel). The product, known as System E.T. 20 (formerly MCW.B 20) is listed on the USEPA's National Contingency Plan (NCP) Product Schedule.

TABLE 4. TPH REDUCTION IN THE INNOVATIVE AND CONVENTIONAL LAND TREATMENT AREAS

Treatment Area	Treatment	Treatment Time (Day Number)	Reduction in TPH (Percent)	
			Estimated From Initial and Final Data	Estimated From Model
A	Bacterial enzyme	0 to 120	69.7	67.1
B	Inorganic/trace organic nutrient and selected bacterial strain mixture	0 to 120	62.8	67.1
[1]C	Oleophilic nutrient/ selected bacterial strain mixture	30 to 120	80.8	80.9
D	Conventional land treatment	0 to 120	67.1	67.1

[1]Substantially greater percent reduction in TPH concentration in Area C in only 75 percent of the time allowed for the other treatments

CONCLUSIONS

Innovative treatment in Area C (oleophilic nutrient / selected bacterial strain mixture) was more effective in treating TPH than innovative treatment in Areas A and B and conventional treatment in Area D. In ITA C, ~80% reduction in TPH was obtained over a 90 day treatment period (i.e., in only 75% of the time allowed for the other treatments). In Areas A, B, and D, ~67% reduction in TPH was obtained over a 120 day treatment period. The first-order rate of biological treatment of TPH in ITA C was about twice that obtained in the other areas. The effectiveness in treating TPH in ITAs A and B was not significantly different than in treating TPH in CTA D.

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